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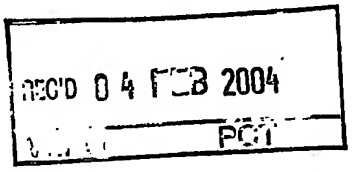

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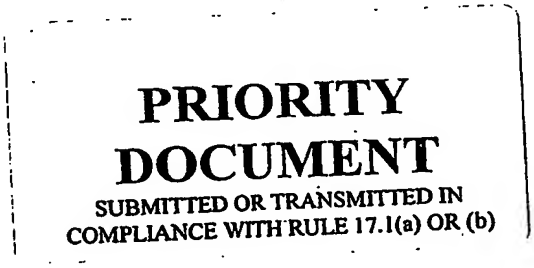
Patentanmeldung Nr. Patent application No. Demande de brevet n°

02027119.3



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Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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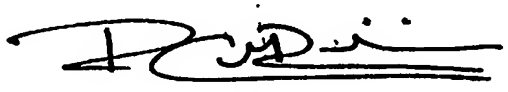

R C van Dijk

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Quaternary ammonium composition

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Clariant International Ltd . 2002DE442 Dr. OT/sch

Description

Quaternary ammonium composition

Use of quaternary ammonium compounds in detergents formulations has been widely used as it improves physical and chemical properties of the mixture.

One of the most used ammonium quaternary are the Hydroxyethyl Quats. They could be classified as a typical cationic surfactant which solubility or hydrophilic characteristics are improved by the presence of a hydroxyl group in its structure. This characteristic makes possible its use in typical anionic formulation in which is stable and shows particular benefits of synergetic action on removal of difficult stains like oily and fatty ones from fabrics or other surfaces, also after aging.

It also presents synergistic effect when incorporate with anionics, amphoterics, and/or non-ionics surfactants.

Hydroxyethyl Quats are detergency boosters for use in all laundry detergent powders and liquid for clothes washing in house hold, industrial, and institutional area.

The use of these compounds in HDP formulations improves the fatty-soil and clay-soil removal, the graying inhibition, the enzyme efficiency and the bleach effects. Besides that it reduces interference of surfactant system on the action of dye transfer inhibitor and dye fixing agents.

All these benefits are described in US 5.415.812, WO 97/45513, WO 97/43367, WO 97/42292, WO 97/44419,WO97/12018, WO 98/13448, WO 98/13449, WO 98/13451, WO 98/13452, WO 98/13453,WO 98/17751, WO 98/17754, WO 98/17755, WO 98/17758, WO 98/17759, WO 98/17766, WO98/17767,

WO 98/17768, WO 98/17769, WO 98/20092,WO 98/35004.

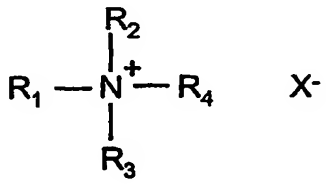
Hydroxyethyl Quats also provide a sensitive synergic improvement in physical and chemical properties of light duty liquid formulations, as described in WO0188073. In Hard Surface Cleaners the Hydroxyethyl Quats increase the detergency when it is in the presence of anionic surfactants and in Disinfectant Cleaners it presents all benefits as comparable with anionic cleaners but with a special anti-bacteria effect, as described in WO 0194511.

The up dated technology available to produce this kind of surfactant is based on synthesis in aqueous medium, as the active content is a salt and so it's highly soluble in water. Therefore, it has been commercialized in aqueous solution. However, nowadays the detergent market tends to use raw materials as concentrated as possible, what means with the lowest amount of water possible. In most of the cases the water has to be removed from the final formulation. So, it's a big advantage to the customer buying the cationic compound obtained in a medium that is part of the final product and don't need to be removed. Besides that, using detergents having high concentrations of detersive substances minimize transportation, storage and packaging costs. It also improves handling for the customer.

In this way detergents having big amounts of water constitute a difficulty for detergent industries because it decreases the content of the active substances.

The present invention provides for quaternary ammonium composition essentially consisting of

a) a cationic compound with general formula:



wherein R_1 is C_8-C_{22}-alkyl, C_8-C_{22}-alkenyl, C_8-C_{22}-alkylamidopropyl, C_8-C_{22}-alkenyl-amidopropyl, C_8-C_{22}-alkyl/alkenyl(poly)alkoxyalkyl, C_8-C_{22}-alkanoylethyl or C_8-C_{22}-alkenoylethyl, R_2, R_3 and R_4 are C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl or a group of the formula $-A-(OA)_n-OH$, A is $-C_2H_4-$ and/or $-C_3H_6-$, n is a number from 0 to 20 and X is an anion,

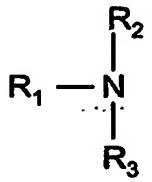
b) water and

c) a non-ionic solvent of the general formula $R-O-(AO)_nH$, where R is hydrogen, alkyl or alkenyl containing 8 to 22 carbon atoms, or phenyl, A is C_2H_4 and/or C_3H_6 and n is a number from 0 to 20, which composition is characterized in that it contains less than 20 % by weight of water.

The quaternary ammonium composition presents 5 to 60 % of an active cationic component a) less than 20 % of water and 40 to 95 % of one or more of the non-ionic solvent. The compound is also characterized for having less than 5 % of by products (free amine plus amine chlorohydrate).
Addition of some additives to improve product characteristics is also possible.

The compositions as claimed herein are prepared in the following way according to the nature of R_2, R_3 and R_4.

If R_4 is an alkyl or alkenyl group an amine of the formula



wherein R_1, R_2 and R_3 are as defined above, is quaternized by reacting it with a halo alkyl or halo alkenyl of the formula R_4-X wherein X is chlorine or bromine. This reaction is made in the presence of a non-ionic solvent c) as defined above. The reaction time is

from 3 to 8 hours and the reaction temperature is from 20 to 100°C. This reaction is done by diluting the starting amine with the non-ionic solvent and then adding the halo alkyl or halo alkenyl compound. It is also possible to first mix the halo alkyl or halo alkenyl compound with the non-ionic solvent and than add the amine.

If a composition is made containing a quaternary compound wherein R_4 is a group of the formula -A-$(OA)_n$-OH, the amine of the formula $R_1R_2R_3N$ is treated with an inorganic halo acid such as for example hydrochloric acid. This reaction is done in the presence of the non-ionic solvent as defined above. The reaction normally is completed after 0,5 to 2 hour at a temperature of 20 to 100°C. In a second step the ammonium salt obtained in the first step is reacted with ethylene oxide and/or propylene oxide at 40 to 100°C

Normally this step takes 3-8 hours, depending on the amount of starting material and the equipment where the reaction is performance.
It's important to emphasize that the component or component used as reactional medium must be inert, what means they cannot react with ethylene oxide or propylene oxide under the theses conditions.

As cationic surfactants there may be used the following ones, alkyldimethyl-hydroxyethyl-ammonium, alkyl-dimethyl(poly)alkoxyalkyl-ammonium, alkyltrimethyl-ammonium, dialkyldimethyl-ammonium, dialkyl-methyl(poly)alkoxyalkyl-ammonium, alkyl-di(poly)-alkoxyalkyl-methyl-ammonium, dialkyl-di(poly)alkoxy-ammonium, alkyl-tri(poly)-alkoxy-ammonium, alkylamidopropyl-trimethyl-ammonium, alkylamidopropyl-dimethyl(poly)-alkoxyalkyl-ammonium, alkoxyethyl-trimethyl-ammonium. Instead of alkyl these ammonium compounds may also have alkenyl groups or mixtures of both. The alkyl as well as the alkenyl groups may contain 8 to 22 carbon atoms. They may be linear or branched. (Poly)-alkoxyalkyl means a group of the formula -A-$(OA)_n$-OH wherein A is ethylene or propylene group or a mixture of both and n is a number of from 0 to 20. Preferably n is zero and A is ethylene that means those compounds and preferred which contain a hydroxyethyl group. Most preferred ammonium compounds are C_8-C_{22}-alkyl- or alkenyl-dimethyl-hydroxyethyl-ammonium compounds. All

mentioned ammonium compounds might contain any kind of anion; the preferred ones are chloride, bromide, acetate, lactate, sulphate or methosulphate.

As solvent there may be used the following ones, an alcohol or an ethoxylated alcohol with general formula $R\text{-}O\text{-}(AO)_nH$, where R is alkyl or alkenyl group containing 8 to 22 carbon atoms, A is C_2H_4 and/or C_3H_6 and n is a number from 0 to 20, a polymer or a block co-polymer with general formula $\text{-}A\text{-}(OA)_n\text{-}OH$ wherein A is ethylene and/or propylene group or a mixture of both and n is a number of from 0 to 20, nonylphenol or ethoxylated nonylphenol with general formula $C_9H_{19}\phi\text{-}O\text{-}(AO)_nH$, where A is C_2H_4 and/or C_3H_6 or a mixture of the compounds above.

Example 1:

To a 3 liter four necked round bottom flask equipped with stirrer, thermometer, reflux condenser and dropping funnel were charged 1460 g of $C_{12}/C_{14}/C_{16}$ alcohol polyglycol 7 EO and 324 g of dimethyl alkyl ($C_{12}/C_{14}/C_{16}$) amine. Under stirring were added 150 g of chloridic acid 34 % in fifteen minutes. Due the exothermicity the temperature reach 70°C. During the addition the temperature was kept between 60-70°C. The system was let under stirring and at 70-75°C for two more hours. We got approx. 1930 g of an intermediate product with the following characteristics:

Appearance (25°C): Clear slightly yellow liquid
Free amine: 0,19 %
Amine Chlorohydrate: 19,0 %
Water (KF): 5,4 %

To a 2 liter high-pressure reactor equipped with stirrer, thermometer, nitrogen feed and pressured dropping funnel were charged 969 g of the intermediate (Amine Chlorohydrate). The system was in inert mode and then heated to 65-70°C. Then 36,7 g (0,75 mols) of ethylene oxide were added in 4 hours, keeping the temperature at

75-80°C and the pressure between 0,5 and 3,0 Bar. We kept the system for 1 more hour stirring at 75-80°C. We got approx. 1005 g of final product with the following characteristics:

Appearance (25°C): Clear slightly yellow liquid
Free amine + amine chlorohydrate: 0,54 %
Active content: 19,5 %
Water (KF): 4,9 %

To decrease even more the amount of water the product was distilled under vacuum and at 70-80°C for 3 hour and we got a product with the following characteristic:

Appearance (25°C): Clear slightly yellow liquid
Free amine + amine chlorohydrate: 0,55 %
Active content: 19,8 %
Water (KF): 1,7 %

Keeping distilling for two more hours at the same conditions we got the following product:

Appearance (25°C): Cloud white liquid
Free amine + amine chlorohydrate: 0,60 %
Active content: 20,3 %
Water (KF): 0,46 %

Summarizing with this process we got tree different possible final product:

Characteristics	Example 1.1	Example 1.2	Example 1.3
Appearance (25°C)	Clear slightly yellow liquid	Clear slightly yellow liquid	Cloud white liquid
Free Amine + Amine Chlorohydrate (%)	0,19	0,55	0,60
Cationic Content (%)	19,5	19,8	20,3
Water (KF) (%)	5,4	1,7	0,46

Example 2:

To a 3 liter four necked round bottom flask equipped with stirrer, thermometer, reflux condenser and dropping funnel were charged 1650 g of $C_{12}/C_{14}/C_{16}$ alcohol polyglycol 7 EO and 905 g of dimethyl alkyl ($C_{12}/C_{14}/C_{16}$) amine. Under stirring were added 419g of chloridic acid 34 % in fifteen minutes. Due the exothermicity the temperature reach 70°C. During the addition the temperature was kept between 60-70°C. The system was let under stirring and at 70-75°C for two more hours. We got approx. 2974 g of an intermediate product with the following characteristics:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days.
Free amine: 0,13 %
Amine Chlorohydrate: 34,6 %
Water: 10,8 %

To a 2 liter high-pressure reactor equipped with stirrer, thermometer, nitrogen feed and pressured dropping funnel were charged 1120 g of the intermediate (Amine Chlorohydrate). The system was in inert mode and then heated to 65-70°C. Then 73,7 g (1,68mols) of ethylene oxide were added in 4 hours, keeping the temperature at

75-80°C and the pressure between 0,5 and 3,0 Bar. We kept the system for 1 more hour stirring at 75-80°C. We got approx. 1005 g of final product with the following characteristics:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days. The product can be easily homogenized by stirring at a temperature between 25 and 50°C.
Free amine + amine chlorohydrate: 0,42 %
Active content: 37,2 %
Water (KF): 9,6 %

To decrease even more the amount of water the product was distilled under vacuum and at 70-80°C for 3 hour and we got a product with the following characteristic:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days. The product can be easily homogenized by stirring at a temperature between 25 and 50°C.
Free amine + amine chlorohydrate: 0,4 %
Active content: 39,7 %
Water (KF): 4,6 %

Example 3:

To a 3 liter four necked round bottom flask equipped with stirrer, thermometer, reflux condenser and dropping funnel were charged 1320 g of $C_{12}/C_{14}/C_{16}$ alcohol polyglycol 7 EO and 456 g of dimethyl alkyl ($C_{12}/C_{14}/C_{16}$) amine. Under stirring were added 211 g of chloridric acid 34 % in fifteen minutes. Due the exothermicity the temperature reach 70°C. During the addition the temperature was kept between 60-70°C. The system was let under stirring and at 70-75°C for two more hours. We got approx. 1930 g of an intermediate product with the following characteristics:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days.
Free amine: 0,10 %
Amine Chlorohydrate: 26,4 %
Water: 8,6 %

To a 2 liter high-pressure reactor equipped with stirrer, thermometer, nitrogen feed and pressured dropping funnel were charged 987 g of the intermediate (Amine Chlorohydrate). The system was in inert mode then heated to 65-70°C. Then 50,3 g (1,14 mols) of ethylene oxide were added in 4 hours, keeping the temperature at 75-80°C and the pressure between 0,5 and 3,0 Bar. We kept the system for 1 more hour stirring at 75-80°C. We got approx. 1005 g of final product with the following characteristics:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days. The product can be easily homogenized by stirring at a temperature between 25 and 50°C.
Free amine + amine chlorohydrate: 0,37 %
Active content: 28,4 %
Water (KF): 7,5 %

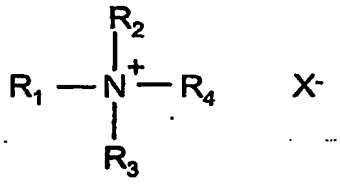
To decrease even more the amount of water the product was distilled under vacuum and at 70-80°C for 3 hour and we got a product with the following characteristic:

Appearance (25°C): Slightly cloud and yellow liquid with shows phase separation after some days. The product can be easily homogenized by stirring at a temperature between 25 and 50°C.
Free amine + amine chlorohydrate: 0,29 %
Active content: 30,1 %
Water (KF): 4,3 %

Claims:

1. A quaternary ammonium composition essentially consisting of

a) a cationic compound with general formula:



wherein R_1 is C_8-C_{22}-alkyl, C_8-C_{22}-alkenyl, C_8-C_{22}-alkylamidopropyl, C_8-C_{22}-alkenyl-amidopropyl, C_8-C_{22}-alkyl/alkenyl(poly)alkoxyalkyl, C_8-C_{22}-alkanoylethyl or C_8-C_{22}-alkenoylethyl, R_2, R_3 and R_4 are C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl or a group of the formula -A-$(OA)_n$-OH, A is -C_2H_4- and/or -C_3H_6-, n is a number from 0 to 20 and X is an anion,

b) water and

c) a non-ionic solvent of the general formula R-O-$(AO)_nH$, where R is hydrogen, alkyl or alkenyl containing 8 to 22 carbon atoms, or phenyl, A is C_2H_4 and/or C_3H_6 and n is a number from 0 to 20, which composition is characterized in that it contains less than 20 % by weight of water.

2. Composition, according to claim 1, which contains 5 to 60 % of the cationic compound a).

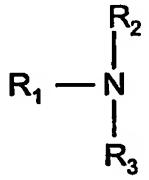
3. Composition, according to claim 1, wherein the cationic compound a) is an C_8-C_{22}-alkyl or C_8-C_{22}-alkenyl-dimethyl-hydroxyethyl ammonium.

4. Composition, according to claim 1, which has 40 to 95 % of the non ionic solvent c).

5. Composition, according to claim 1, which has less than 5% of by-products (free amine plus amine chlorohydrate).

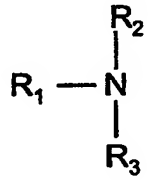
6. Composition, according to claim 1, which the non ionic solvent is an ethoxylated fatty alcohol, a fatty alcohol, a polyethylene glycol, a polypropylene glycol, a block co-polymer of ethylene and propylene, a nonylphenol, a ethoxylated nonylphenol or a mix of these compounds.

7. A process for preparing a composition as claimed in claim 1 wherein R_4 in the compound a) is defined as C_1-C_{22}-alkyl or C_2-C_{22}-alkenyl, which process consists in reacting an amine of the formula



wherein R_1, R_2 and R_3 are as defined above with a halo alkyl or halo alkenyl of the formula R_4-X wherein R_4 is C_1-C_{22}-alkyl or C_2-C_{22}-alkenyl and X is chlorine or bromine in the presence of a non-ionic solvent c) as defined in claim 1.

8. A process for preparing a composition as claimed in claim 1 wherein R_4 in the cationic compound a) is defined as a group of the formula -A-$(OA)_n$OH wherein A and n are as defined in claim 1, which process consists of reacting an amine of the formula



with an inorganic halo acid and than reacting the ammonium salt thus obtained with ethylene oxide and/or propylene oxide.

9. Process according to claim 7 or 8, wherein the amine is C_8-C_{22}-alkyl or C_8-C_{22}-alkenyl-dimethyl amine.

10. Process, according to claim 8, wherein the monohalo acid is aqueous, hydrochloric acid.

11. Process, according to claim 8, wherein the ammonium salt is reacted with ethylene oxide.

12. Process according to claim 8, wherein the non ionic solvent is Coconut PEG 7.

13. Process according to claim 8, wherein the first step is proceed in a temperature between 20 and 100°C.

14. Process according to claim 8, wherein the second step is proceeded in a temperature between 40 and 100°C.